INVESTIGATION OF THE OPTICAL AND OPTOELECTRONIC PROPERTIES OF GASE AND ITS HETEROJUNCTIONS FOR PHOTODETECTOR APPLICATIONS

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Investigation of the Optical and Optoelectronic Properties of GaSe and its Heterojunctions for Photodetector Applications

by

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Dedicated to my family

Certificate

This is to certify that the thesis entitled **“Investigation of the Optical and Optoelectronic Properties of GaSe and its Heterojunctions for Photodetector Applications”** being submitted by **Mr. Sahin Sorifi** to **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. He has worked under my guidance and supervision and has fulfilled the requirements, which to our knowledge have reached the requisite standard for the submission of the thesis.

The results contained in this thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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Abstract

Gallium selenide (GaSe), a III−VI semiconducting layered material from the metal monochalcogenide (MMC) family, has demonstrated tremendous potential in the fields of optoelectronics, nonlinear optics, and tera hertz radiation with its many intriguing properties. Currently, various theoretical and experimental research on GaSe has shown a number of unique characteristics as the bulk GaSe crystals have been systematically reduced to mono or few layers. The bandgap tunability of the GaSe crystal has also been anticipated theoretically by varying the number of layers or by applying mechanical strain. Ultrathin flakes of GaSe can be produced from bulk GaSe crystal by using the mechanical exfoliation method and the exfoliated flakes possess a very good crystallinity and few defects. Therefore, exfoliated GaSe nanoflakes based field effect transistors (FETs) and photodetectors exhibit excellent electrical and optical performance, revealing its great potential to advance the development of electronic and optoelectronic devices.

In the initial part of the proposed thesis work, we explored the high-temperature robustness of the GaSe-based metal-semiconductor-metal (MSM) photodetector. Due to the direct bandgap nature of GaSe flakes in their few or multilayer forms, GaSe-based devices were found to show excellent photoresponse. Although, several reports were available on the performance of these GaSe-based devices at room temperature, their high-temperature behaviour was unknown. Hence, we took a mechanically exfoliated GaSe nanosheet and fabricated an MSM photodetector to conduct a comparative study of the performance of a GaSe-based device at both room and high temperatures. The photoresponsivity, detectivity and external quantum efficiency were measured to be 2.6 A/W, 1.0×10^{12} Jones and 850% respectively at room temperature. The photodetector maintained its photoresponse and thermal stability up to a high temperature of 120 °C, giving out a high photoresponsivity of 4.5 A/W.

Optimizing the performance of nanostructured optoelectronic devices requires a careful consideration of the thickness-dependent optical and optoelectronic properties. GaSe flakes shows a color variation depending on their thicknesses and that can be utilized in sampling GaSe flakes with different thicknesses. It is observed that multilayered GaSe flakes show degradation in their optical and optoelectronic properties when reduced down to thinner layers. The thinner GaSe layers are prone to environmental degradation because of the surface oxidation, which is responsible for the poor performance of the thinner GaSe layer-based

photodetectors. Although several studies on the study of multilayered GaSe flakes with random thicknesses are separately available, a comprehensive analysis of the behaviour of GaSe flakes with varying thickness is still lacking. Consequently, we carried out a systematic investigation of the thickness-dependent optical and optoelectronic properties of mechanically exfoliated GaSe ultrathin films.

2D/3D heterojunctions between 2D layered materials and typical 3D materials such as Si, Ga_2O_3, or SiC have shown enormous promise for large-scale practical applications such as photodetectors and highly efficient solar cells. Until now, the majority of reported 2D/3D p-n heterojunction-based photodetectors were limited to the combination of Si and graphene, or with transition metal dichalcogenides (TMDCs) such as MoS_2, and only a few by the combination of graphene and GaN. There are hardly any reports available on p-n heterojunctions based on 3D Si or Ga_2O_3 and 2D MMCs like InSe and GaSe.

We have made a vertical GaSe/Si p-n heterojunction by directly transferring the GaSe flake onto the Si substrate via mechanical exfoliation. One contact is taken from the top layer of GaSe flake and the other contact is taken from the bottom layer of Si substrate, thereby making an arrangement for current transport through a vertical channel. This vertical structure effectively reduces the transport channel length and probability of recombination. Hence, the net carrier collection efficiency gets enhanced. The GaSe/Si heterostructure device shows an excellent performance with a high photoresponsivity, specific detectivity, and EQE value of ~2.8×10^3 A/W, 6.2×10^{12} Jones, and 6011, respectively, at a biasing of -5V. In addition, a strong photoresponse of 6 A/W, obtained at zero bias, shows that the heterojunction device can operate without any external power. These results indicate that the self-biased GaSe/Si heterostructure device has a great potential in the field of photodetection.

In the last part of the thesis work, a detailed investigation has been done on the GaSe/Ga_2O_3-based vertical heterojunction. Kelvin probe force microscopy (KPFM) measurements at the hetero-interface provides the surface potential difference between Ga_2O_3 and GaSe, which is used to calculate the conduction band offset value. Based on the derived value of conduction band offset, energy band diagrams are drawn for the GaSe/Ga_2O_3 heterojunction. With the help of these band diagrams, the current transport mechanism and the photoresponse properties of the GaSe/Ga_2O_3 heterojunction device are explained.

सार

गैलियम सेलेनाइड (GaSe) एक III-VI अर्धचाल्कोजन लेयरबद्ध सामग्री है जो मेटल मोनोकैलकोजनाइड (MMC) परिवार से है, और इसमें विकीर्ण गुणों के साथ ऑप्टोइलेक्ट्रोनिक्स, असंचित ऑप्टिक्स, और तेराहर्ट्ज़ विकिरण के क्षेत्र में बड़ी संभावना दिखाई दी है। वर्तमान में, GaSe पर विभिन्न सैद्धांतिक और प्रायोगिक शोध ने बुल्क GaSe क्रिस्टल को सिस्टमैटिक रूप से मोनो या कुछ ही लेयर्स में कम कर दिया है। लेयरों की संख्या को बदलकर या यांत्रिक तनाव लगाकर थियोरेटिकल रूप से भी GaSe क्रिस्टल के बैंडगैप को बदलने की संभावना भी थी। यांत्रिक उनमाकों से बुल्क GaSe क्रिस्टल से गैसे के अल्प पत्तियां बना सकते हैं और इन पत्तियों में बहुत अच्छी क्रिस्टलिनता और कुछ दोष होते हैं। इसलिए, तंत्रिका पृष्ठ प्रभाव ट्रांजिस्टर (FETs) और फोटोडिटेक्टर आदि में गैसे के अल्प पत्तियों वाले यंत्रित्रों और ऑप्टिकल प्रदर्शन शानदार हैं, जिससे यह इलेक्ट्रॉनिक और ऑप्टोइलेक्ट्रोनिक उपकरणों के विकास में उन्नति का अवसर प्रदर्शित करते हैं।

प्रस्तावित थीसिस के कार्य के प्रारंभिक भाग में, हमने गैसे के आधारित धातु-अर्धधातु-धातु (MSM) फोटोडिटेक्टर की उच्च तापमान स्थिरता की अनुसंधान किया। गैसे के कुछ या बहुलेयर रूपों में सीधा बैंडगैप प्रकृति के कारण, गैसे के आधारित यंत्रों में उत्कृष्ट फोटोप्रतिसाद प्रदर्शित होता है। हालांकि, कई रिपोर्ट उपलब्ध थे जो इन गैसे के आधारित यंत्रों के प्रदर्शन को कमरूम तापमान पर दिखा रहे थे, उनके उच्च तापमान व्यवहार के बारे में जानकारी नहीं थी। इसलिए, हमने एक यांत्रिक रूप से गैसे के अल्प पत्ती को लिया और एक MSM फोटोडिटेक्टर बनाया ताकि एक गैसे के आधारित यंत्र के प्रदर्शन के तुलनात्मक अध्ययन को कमरूम और उच्च तापमान दोनों में कर सकें। फोटोप्रतिसाद, डिटेक्टिविटी और बाह्यंत्री क्वेंटम दक्षता को रुम तापमान पर 2.6 A/W, 1×10^{12} Jones, और 850% क्रमश: मापा गया। फोटोडिटेक्टर ने अपने फोटोप्रतिसाद और तापमानिक स्थिरता को 120 °C तक बनाए रखा, जिससे उसने 4.5 A/W का उच्च फोटोप्रतिसाद दिया।

नैनोसंरचित ऑप्टोइलेक्ट्रोनिक यंत्रों के प्रदर्शन को सरताज़ी करने के लिए मोटाई-आधारित ऑप्टिकल और ऑप्टोइलेक्ट्रोनिक गुणों का सतर्क ध्यान देने की आवश्यकता होती है। गैसे की पत्तियां अपनी मोटाई के आधार पर रंग के भेदभाव को दिखाती हैं और उन्हें विभिन्न मोटाइयों के साथ नमूने लेने में इस्तेमाल किया जा सकता है। यह देखा गया है कि कई-चरणीय GaSe पत्तियां अपनी ऑप्टिकल और ऑप्टोइलेक्ट्रोनिक गुणों में गिरावट दिखाती हैं जब उन्हें पतली लेयरों में कम किया जाता है। पतली GaSe लेयरें परतों के सतहीकरण के कारण पर्यावरणीय गिरावट का शिकार होती हैं, जो पतली GaSe लेयर आधारित

फोटोडिटेक्टरों के खराब प्रदर्शन के लिए जिम्मेदार है। यद्यपि कई अध्ययन अलग-अलग मोटाइयों के साथ कई-चरणीय GaSe पत्तियों के अध्ययन के लिए उपलब्ध हैं, लेकिन अलग-अलग मोटाइयों के साथ GaSe पत्तियों के व्यवहार का विवेचना योग्य विश्लेषण अभी भी अनुपलब्ध है। इसलिए, हमने तांत्रिक रूप से गैसे के अल्प पत्तियों की मोटाई-आधारित ऑप्टिकल और ऑप्टोइलेक्ट्रोनिक गुणों के विश्लेषण की एक सिस्टमैटिक जांच की।

2D/3D विषम-संधि द्वारा 2D लेयरबद्ध सामग्री और पारंपरिक 3D सामग्री जैसे Si, Ga_2O_3 या SiC के बीच हुए संधि का उपयोग फोटोडिटेक्टर और उच्च दक्ष सौर सेल जैसे बड़े मापदंडियों के अनुप्रयोगों के लिए बड़े वादे का प्रदर्शन किया है। अब तक, 2D/3D p-n संधि आधारित फोटोडिटेक्टरों की अधिकांश रिपोर्ट लिमिटेड सी और ग्रेफेन, या MoS_2 जैसे पारंपरिक धातुविन्यास या ट्रांजीशन मेटल डाइकेलकोजेनाइड्स (TMDCs) के संयोजन पर ही सीमित थे, और कुछ ही जैसे ग्रेफेन और GaN के संयोजन पर थे। 3D Si या Ga_2O_3 और 2D MMCs जैसे InSe और GaSe के संयोजन पर हुए p-n संधि के बारे में लगभग कोई रिपोर्ट उपलब्ध नहीं है।

हमने तांत्रिक रूप से गैसे परत को सीधे स्थानांतरित करके एक वर्टिकल GaSe/Si p-n संधि बनाई है। गैसे परत के एक संपर्क को गैसे परत के शीर्ष पर से और दूसरे संपर्क को बेस परत के नीचे से लिया गया है, जिससे वर्टिकल चैनल के माध्यम से धारा परिवहन के लिए व्यवस्था बनाई गई है। यह वर्टिकल संरचना परिवहन चैनल की लंबाई को सघन करती है और पुनर्जनन की संभावना को कम करती है। इसलिए, GaSe/Si संधि यंत्र एक उच्च फोटोप्रतिसाद, विशिष्ट डिटेक्टिविटी, और EQE मानयोजन वैल्यू प्रदर्शित करता है, जो कि एक -5 V के बायसिंग में $\sim 2.8 \times 10^3$ A/W, 6.2×10^{12} Jones, और 6011, क्रमशः है। इसके अलावा, शून्य बायस पर प्राप्त 6 A/W की मजबूत फोटोप्रतिसाद, यह दिखाता है कि यंत्र संधि बिना किसी बाह्य शक्ति के चल सकता है। ये परिणाम इस दिखाते हैं कि स्व-धारित GaSe/Si संधि यंत्र फोटोडिटेक्शन के क्षेत्र में बड़ी संभावना रखता है।

थीसिस के अंतिम भाग में, हमने GaSe/Ga_2O_3 पर आधारित वर्टिकल संधि पर विस्तृत अध्ययन किया है। गैसे और Ga_2O_3 के बीच हेटेरो-इंटरफेस पर केल्विन प्रोब फोर्स माइक्रोस्कोपी (KPFM) मापन किए गए हैं, जो Ga_2O_3 और GaSe के बीच सतहीय अंतर के बीच सतहीय पोटेंशियल अंतर को प्रदान करते हैं, जिससे कंडक्शन बैंड ऑफसेट मूल्य की गणना की गई। अभिगत कंडक्शन बैंड ऑफसेट मूल्य के आधार पर, GaSe/Ga_2O_3 हेटेरोजंक्शन के लिए ऊर्जा बैंड चित्र बनाए गए हैं। इन बैंड चित्रों की मदद से, GaSe/Ga_2O_3 हेटेरोसंरचना यंत्र के धारा परिवहन यांत्रिकी और फोटोप्रतिसाद गुणों की व्याख्या की गई।

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List of Symbols and Abbreviations

Symbols

α	Optical absorption coefficient
A	Effective area of the device
$A*$	Effective Richardson's constant
$D*$	Specific detectivity
e	Charge of an electron
ε	Tensile strain
E_g	Bandgap of the semiconductor
G	Gain in the device
h	Planck's constant
I_{ph}	Photocurrent
I_d	Dark current
I_λ	Illumination current
I_S	Saturation current
k	Boltzmann's constant
P_λ	Incident power density
R_λ	Photoresponsivity
T	Absolute temperature
t	Time
τ	Response time
$\tau_{lifetime}$	Lifetime of holes
$\tau_{transit}$	Transit time
V_a	Applied bias
V_{bi}	Built-in potential
ϕ_{metal}	Work function of the metal
ϕ_{sample}	Work function of the sample
ϕ_B	Barrier potential
ϕ_{tip}	Work function of the tip
ϕ_{GaSe}	Work function of GaSe
$\phi_{Ga_2O_3}$	Work function of Ga_2O_3
ϕ_{Si}	Work function of Si
η	Ideality factor
χ	Electron affinity of the semiconductor
μ	Mobility
ν	Frequency
γ	Gruneisen parameter
ΔE_C	Conduction band offset

Abbreviations

AFM	Atomic Force Microscopy
CVD	Chemical Vapor Deposition
CMP	Chemical Mechanical Polished
CPD	Contact Potential Difference
DI	Deionized
DUT	Device under test
EBL	Electron Beam Lithography
EDS	Energy-dispersive X-ray Spectroscopy
EQE	External quantum efficiency
FESEM	Field Emission Scanning Electron Microscopy
FETs	Field Effect Transistors
GaSe	Gallium Selenide
GaN	Gallium Nitride
Ga_2O_3	Gallium Oxide
hBN	Hexagonal Boron Nitride
IPA	Iso-propyl Alcohol
I-V	Current-Voltage
I-t	Current-Time
KITE	Keithley Interactive Test Environment
KPFM	Kelvin Probe Force Microscopy
LEDs	Light Emitting Diodes
LH	Lift-height
MMCs	Metal monochalcogenides
MoS_2	Molybdenum Disulfide
MSM	Metal-Semiconductor-Metal
NEP	Noise Equivalent Power
PDCR	Photo-to-dark current ratio
PL	Photoluminescence
PMMA	Poly Methyl Meth-Acrylate
PSPD	Position-sensitive Photodetector
SBH	Schottky Barrier Height
SiC	Silicon Carbide
SiO_2	Silicon dioxide
SEM	Scanning Electron Microscopy
SCS	Semiconductor Characterization System
SPM	Scanning Probe Microscopy
STM	Scanning Tunneling Microscopy
TDLMs	Two-dimensional layered materials
TMDCs	Transition Metal Dichalcogenides
TE	Thermionic Emission
UV	Ultraviolet

vdW	van der Waals
vdWHs	van der Waals heterostructures
0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional